

Brief Review: Preparation Techniques of Biomass Based Activated Carbon Monolith Electrode for Supercapacitor Applications

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Brief Review: Preparation Techniques of Biomass Based Activated Carbon Monolith Electrode for Supercapacitor Applications

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Abstract. The synthesis of activated carbon monolith electrode made from a biomass material using the hydrolytic pressure or the pelletization technique of pre-carbonized materials is one of standard reported methods. Several steps such as pre-carbonization, milling, chemical activation, hydraulic press, carbonization, physical activation, polishing and washing need to be accomplished in the production of electrodes by this method. This is relatively a long process that need to be simplified. In this paper we present the standard method and proceed with the introduction to several alternative methods in the synthesis of activated carbon monolith electrodes. The alternative methods were emphasized on the selection of suitable biomass materials. All of carbon electrodes prepared by different methods will be analyzed for physical and electrochemical properties. The density, degree of crystallinity, surface morphology are examples for physical study and specific capacitance was an electrochemical properties that has been analysed. This alternative method has offered a specific capacitance in the range of 10 to 171 F/g.

INTRODUCTION

Carbon monolith (CM) is a type of carbon that is studied widely because it has advantages in electrical and mechanical properties [1]. The CM can be made from a various raw materials such as conductive polymers, petroleum coke and biomass. Some biomass materials after the drying, followed by milling and sieving process show the self-adhesive properties. One of the most common methods reported in CM manufacturing involves the following steps: (a) pre-carbonization, (b) milling, (c) chemical activation, (d) pelletization, (e) carbonization and (f) physical activation. This CM production technique has been used in several biomass materials such as oil palm empty fruit bunches [2], rubber wood sawdust [3] and sugarcane bagasse [4]. The CM characteristics show typically low density, high surface area and strong mechanical structure. These CM properties is suitable for its use as an electrode in energy storage devices such as a supercapacitors. The capacitive properties of CM electrodes from oil palm empty fruit bunches, sugarcane bagasse and rubber wood sawdust shows good performance as a supercapacitor electrode. However, in the process of CM production steps above takes relatively a long time, so it needs to be simplified. The suitable biomass material precursor can be used to modify the production process so that some of the above steps can be eliminated. This paper demonstrates some alternative techniques in preparing monoliths of activated carbon made from biomass materials. The performance of carbon monoliths is reviewed on the basis of capacitive properties when it used as an electrodes in supercapacitor devices.

THE PRODUCTION TECHNIQUE OF CARBON MONOLITHS

Six CM production techniques from several biomass materials are shown in Table 1. Description of the T1 to T6 production technique was included in this table. The differences in every techniques are based on the simplification

of T1. T2 presents a simplification of T1 with the integration of the carbonization step and the physical activation. The raw material for T1 technique generally can be used in T2 technique. T3 is a technique offered by changing and eliminating some steps in T1, this technique has been tried on the production of carbon monolith from banana peel. T4 is a technique that is presented using an original material that has become carbon, like carbon from a coconut shell. This technique has advantages such as to fabricate a supercapacitor electrode in monolith form with flexible mechanic properties. The main rule in this method is that activated carbon is sprayed on both sides of the separator material to form a complete supercapacitor cell. T5 it is a simplification of T1 with the elimination of the milling process, this technique is provided to maintain the existing pore structure naturally in a certain biomass materials. In this review it has been used on the rubber wood chunk. T6 is the most concise process in the production of CM, the sample is naturally stacked and molded into pellets through the compression process and continued with carbonization and activation processes. T6 technique has been performed on spiderweb samples.

TABLE 1. The CM production techniques and its description

Technique	Full description
T1	Pre-carbonization, milling, chemical activation, pelletization, carbonization, physical activation
T2	Pre-carbonization, milling, chemical activation, pelletization, carbonization-physical activation
T3	Milling, casting technique, pre-carbonization, carbonization, physical activation
T4	Milling, chemical activation and spraying
T5	Pre-carbonization, pelletization and carbonization-physical activation
T6	Pelletization and carbonization-physical activation

RESULTS AND DISCUSSION

Table 2 shows the crystallinity properties of CM samples produced in various techniques. For all samples indicated that the 2θ angle is appropriate to indicate the presence of carbon material at scattering angles of $23-26^\circ$ and $43-46^\circ$. This scattering angle have a correlation with (d_{002}) and (d_{100}) interlayer spacing in range of 0.33-0.37 nm and 0.19-0.20 nm. The stack height (L_c) and stack width (L_a) data show irregular nature, where L_c is in the range of 0.76-1.14 nm and L_a in the range of 0.19-2.29 nm. The data in Table 1 illustrates that the difference in the production technique has no significant effect on the crystalline properties of the resulting monolithic carbon electrodes. This fact shows that various production techniques can be developed by considering the compatibility of the raw material with the techniques reserved.

Figure 1 shows the SEM micrograph for the samples provided with T1, T3, T4, T5 and T6 production techniques. T2 techniques are not shown because this techniques display almost similar SEM morphology as T1. The SEM image clearly shows the difference between sample 1a and other samples. Figure 1a shows that the carbon particles are clearly visible with high density, irregular particle shape accompanied by the presence of pores between particles. This result is clearly related to the process of milling, sieving and compression prior to carbonization and activation processes. Figure 1b shows the SEM micrograph for the carbon electrode made from sugarcane bagasse provided by the T1 technique. It is shown that the sample particles are regularly shaped so that the pores between the particles are more open. The electrodes from bagasse show different morphological characteristics with electrode samples from rubber wood sawdust. Figure 1c shows a sample of carbon from a banana peel provided by T3. This 1c image shows the surface morphology of the electrode is bonded with particles together, so the space between the particles is not clearly apparent. This result is due to the production technique of T3 by casting a sample of banana peel sludge after the milling process using a blender and then dried causing the reformtion of particles to bind after being dried. Figure 1d shows carbon samples from coconut shell through T4 technique. T4 technique uses a spraying method in production of CM electrode. This image shows that the spraying rule is also good for producing CM electrode. While T5 and T6 techniques were developed with the aim of maintaining the special features of the raw material used in the manufacture of carbon monoliths electrode. Figure 1e shows the resulting electrode clearly retains the natural pore properties that already present in the wood sample and these pores play a positive role in the process of ion diffusion into the meso and micro pores of the electrode. Figure 1f shows the nature of the spiderweb sample already available in the form of micro fiber. T6 technique can maintain this microfiber structure to show its own advantages in the resulting electrode. All data shown in Fig. 1 demonstrates the uniqueness of each method developed.

TABLE 2. Crystallinity properties : diffraction angle 2θ , interlayer spacing d , stack high and (L_c) and stack width (L_a) for some biomass materials, rubber wood sawdust (RWSD), sugarcane bagasse (SB), oil palm empty fruit bunches (EFB), banana peel (BP), charcoal from coconut shell (CC), rubber wood (RW) and spider web (SW), all samples are carbonized and activated at the same temperature.

T	$2\theta_{200}$ ($^{\circ}$)	$2\theta_{001}$ ($^{\circ}$)	d_{002} (nm)	d_{100} (nm)	L_c (nm)	L_a (nm)	RM	Ref
T1	23.98	44.59	0.37	0.20	1.14	2.28	RWSD	[5]
T1	24.42	45.52	0.36	0.19	0.85	2.16	SCB	[4]
T2	24.53	44.73	0.36	0.20	1.12	2.23	EFB	[6]
T3	26.58	46.44	0.33	0.19	0.98	0.91	BP	[7]
T4	24.65	45.43	0.36	0.19	1.05	1.20	CC	[10]
T5	25.74	43.67	0.36	0.20	0.76	2.29	RW	[11]
T6	26.06	43.97	-	-	-	-	SW	[12]

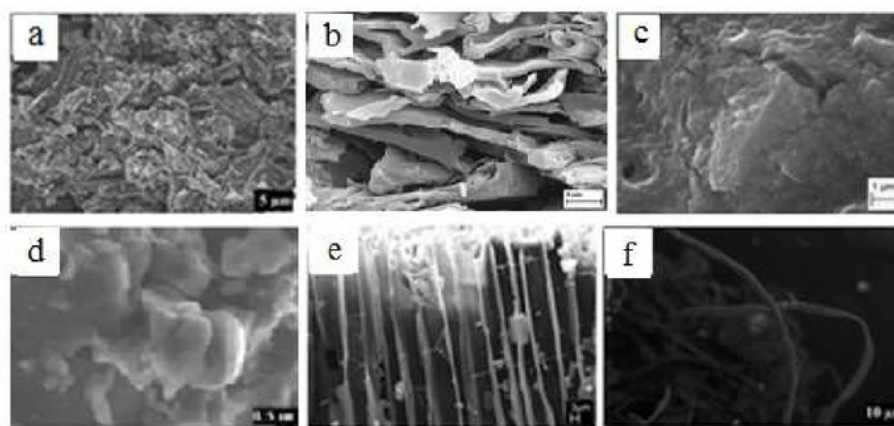


FIGURE 1. SEM micrographs for the samples representing different production method from varies of biomass material such as T1 for rubber sawdust (RWSD) (a), T1 for biomass material of bagasse (SB) (b), T3 for banana peel biomass material (BP) (c), T4 for the biomass material of the coconut shell (CC) (d), T5 for rubber wood (RW) (e) and T6 for spider web (SW) (f).

Table 3 shows density, surface area and specific capacitance of the supercapacitor electrodes obtained by different production techniques. The technique T1 and T3 shows nearly the same density. The density of the electrode is related to the surface area of the sample. T1 and T3 samples display almost the same surface area. This result also corresponds to the cell-specific capacitance, in contrast to the SC samples provided with the T1 technique displaying a higher specific capacitance despite showing almost the same density. The difference in the specific capacitance of this sample is enhanced by the more availability of pore between the particles compared to the RWSD samples, this result can be observed in Figs. 1a and 1b. Another uniqueness influenced by the nature of the SC sample is uniform particle shape resulting with a slightly higher density. The lowest density is shown by the sample produced with the T5 technique. This result is clearly supported by the morphological form of the sample with regular and elongated pores on all parts of the sample. This pore characteristics produces good capacitive properties even with relatively lower surface area. The samples provided with the T2 technique i.e., the samples provided from the empty fruit bunches of oil palm display unique properties. This sample has the highest density but shows the specific capacitance which is relatively same as the sample provided from the banana peel. The capacitive uniqueness of the electrode is the combination properties of pore and conductivity. The T2 sample shows a high density that has advantage for the electrical conductivity properties of the electrode. It has been demonstrated that the production technique developed electrodes carbon monolith with a combination of good physical and electrochemical properties.

TABLE 3. Density (ρ), surface area (S_{BET}), specific capacitance of carbon electrodes made from rubber wood sawdust (RWSD), sugarcane bagasse (SB), oil palm empty bunch (EFB), banana peel (BP), Coconut shell (CC), rubber wood (RW) and spider web (SW).

T	P (gr/cm^3)	S_{BET} (m^2/g)	C_{sp} (F/g)	RM	Ref
T1	0.69	534	54	RWSD	[5]
T1	0.74	-	171	SB	[4]
T2	1.89	-	66	EFB	[6]
T3	0.65*	581	68	BP	[7]*[8]
T4	-	194	10	CC	[9]
T5	0.30	331	115	RW	[11]

CONCLUSION

Various techniques for the production of carbon monolith electrodes have demonstrated good physical and electrochemical properties. Differences in production technique do not present a clear distinction in the crystalline properties of the sample but provide a different morphological appearance and this it is clearly influenced by the uniqueness of the raw material. Every biomass material selected as precursor material in the manufacture of electrodes exhibits unique properties, so as to provide variations in the density, surface area and specific capacitance of the electrodes. This variation of production technique has opened up space for the selection of new paths in production of carbon monolith based on the superior characteristics of the biomass materials.

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